

ON THE MECHANISM OF METHANOL CONVERSION OVER ZEOLITE

Yoshio Ono

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152, Japan

INTRODUCTION

Zeolites convert methanol into hydrocarbons. The most intriguing problem concerning the mechanism of the conversion is the way of forming carbon-carbon bonds from methanol. Chang and Silvestri(1) proposed the participation of carbenoid species, which is assumed to be produced by a concerted α -elimination mechanism, involving both acidic and basic sites. Kaeding and Butter(2) proposed a mechanism involving the reaction of an incipient methyl carbenium ion from protonated dimethyl ether (or methanol) and the methyl group of dimethyl ether, at which a negative center is created by the aid of an anionic site on the catalyst. The attack of methyl carbenium ion on the C-H bond of methyl group is more stressed in the mechanism involving a pentacoordinated carbon center(3,4), as originally proposed in the polymerization or alkylation of methane in superacid chemistry(5,6). van der Berg et al.(7) suggested that the Stevens-type rearrangement of trimethyl oxonium ion could be the first step of the C-C bond formation. The intermediacy of methyl radical was proposed by Zatorski and Krzyzanowsky(8). Apart from the detailed mechanism of the C-C bond formation, the reaction is suggested to have an autocatalytic character(4,9,10). Here, the origin of the autocatalytic phenomena and its implication for the mechanism is discussed, and then the scheme of the first C-C bond formation is discussed to conclude that "methyl carbenium ion" species is the most plausible intermediate.

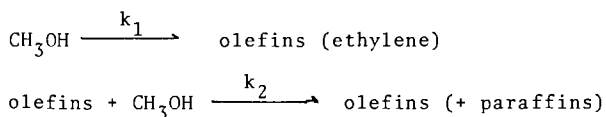
RESULTS AND DISCUSSION

Autocatalytic Phenomena

The autocatalytic behavior of the conversion was first pointed out by Chen and Reagan(9), who noticed that the rate of conversion of methanol was very slow at low conversion levels, but it accelerated rapidly as the concentration of hydrocarbons increased. Another feature of the autocatalysis is observed in the dependence of the hydrocarbon yield on the reaction temperature(10). Thus, the abrupt increase of the hydrocarbon yield is observed in a small temperature range, and the temperature of the jump depends on the acidity of ZSM-5 zeolite. The jump of the hydrocarbon yield with temperature is observed also for the conversion over ferrierite.

The autocatalysis was more clearly visualized in the reaction under low-pressure and low-temperature conditions(4). The reaction was carried out in a gas-recirculation system. At 492 K, only a small amount of hydrocarbons was formed for the first 8 h, though most of methanol was converted into dimethyl ether. After 12 h, the hydrocarbon yield increased abruptly, reaching 80 % at 18 h. At higher temperatures, the reaction proceeded in a similar fashion, but faster. The induction period lasted for 4-5 and 1.5-2 h at 512 and 531 K, respectively. These kinetic features indicate clearly the autocatalytic nature of the conversion.

In order to confirm that the reaction is autocatalytic, some of the reaction products were added to the starting methanol. The addition of ethylene or cis-2-butene (5 % of methanol in moles) decreased the "induction period" to 2 h at 512 K. This is about half of the period in the reaction with pure methanol. On the other hand, the addition of paraffins had no effect on the induction period. Therefore, it is concluded that the autocatalysis is caused by the reaction of methanol and olefins, which is much faster than the reaction to produce incipient olefins. Thus, as proposed by Chen and Reagen(9), the reaction can be divided into the following two steps.



The ratio of the rate constants (k_1/k_2) for the two reactions was estimated as 7×10^{-4} and 1.1×10^{-3} , respectively(4). The abrupt change of the conversion with temperature, as observed in a flow system, may be caused at the temperature, at which the certain amount of olefins is accumulated in a reactor. As for the mechanism, one must consider the two steps separately. The second step, the propagation of the carbon-chain, plausibly involves the electrophilic methylation of olefins, for which Bronsted acid sites are responsible, as first pointed by Anderson et al.(11). The scheme of the first step will be discussed below.

Conversion of Methanol over Nafion-H and Heteropolyacids

To obtain information on the sites responsible for the conversion, the reaction was carried out in a gas-recirculation system over the catalyst with preadsorbed pyridine. Prior to the reaction, the catalyst was exposed to pyridine vapor for 2 h at 473 K, and then evacuated at 512 K for 1 h. The only product observed was dimethyl ether and no hydrocarbons were produced in 47 h. The reaction over Na-ZSM-5 give a similar result. These facts indicates that the acid sites plays a decisive role in the formation of hydrocarbons. This implies that the reaction should proceed also over strongly acidic solid other than zeolites.

Nafion-H, a perfluorinated resin sulfonic acid, is known to have high catalytic activities for the alkylation of benzene with alcohols and the methylation of phenol with methanol, and is reported to be a solid superacid. The conversion of methanol over Nafion-H was examined with a closed-recirculation system(4). Methanol of 7.7×10^5 Pa was introduced over 1 g of Nafion-H at 512 K, and the gas-phase composition was analyzed at appropriate intervals. Dimethyl ether is the only product for the first 2 h, and after 2 h, the rate of hydrocarbon formation was accelerated with time, which is characteristic of an autocatalytic reaction. The fact that the features of the conversion over Nafion-H resembles those over ZSM-5 strongly indicates that Bronsted acid sites are active centers for the conversion.

It was found that dodecatungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), a highly acidic solid, also had high activities for methanol conversion(12).

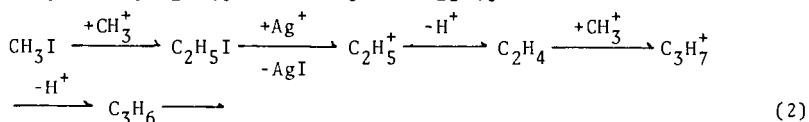
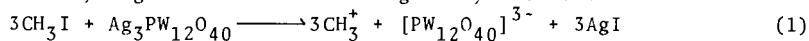
Interaction of Methanol with ZSM-5, Infrared Study

Infrared spectroscopic study revealed that methanol (CD_3OH) reacts with the acidic hydroxyl group of ZSM-5 to form methoxyl group ($\text{CD}_3\text{O}-$) at 423 K. When the zeolite which beared $\text{CD}_3\text{O}-$ groups was heated at 512 K, the CD_3 bands completely disappeared and bands due to O-D stretching appeared, indicating that the desorption of methoxyl groups is accompanied with the cleavage of C-D bonds. The analysis of molecules desorbed from the surface revealed that the decomposition of the methoxyl groups leads to the formation of hydrocarbons.

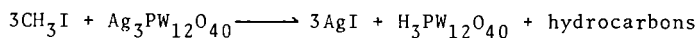
The reaction of the methoxyl group with benzene gave toluene, indicating that the surface methoxyl groups can be a source of "methyl carbenium ions". In other words, the "methoxyl groups" in ZSM-5 could be more properly comprehended as part of a methyl ester of the zeolitic acid than as part of a metal alkoxide, just as a methyl group in dimethyl sulfate, a good methylating agent.

Selfcondensation of Methyl Iodide over $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$

In order to ascertain the role of methyl carbenium ions in the formation of carbon-carbon bonds, the attempt to generate them was made; methyl iodide was reacted with $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$. Methyl carbenium ions were supposed to be generated according to Eq.(1) because of the high tendency of forming silver iodide, and then to attack the carbon-hydrogen bonds of remaining methyl iodide.



The expected overall reaction is summarized as



Experiments were carried out as follows. The powder of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ (0.28 mmol) was reacted with methyl iodide vapor (1.80 mmol) at 423 or 573 K in a closed-recirculation system. The results are given in Table 1. The reaction was almost finished by the time when the first analyses were made, 15 and 5 min for the reaction at 423 and 573 K, respectively, the only minor change in the gas-phase composition being observed thereafter. About 3 moles of methyl iodide disappeared from the gas phase, and, at the same time, most of carbon atoms from consumed methyl iodide appeared as hydrocarbons, as was expected from Eq.(2). It should be noted that methyl iodide does not convert into hydrocarbons over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ or ZSM-5 even at 573 K. At 573 K, the distribution of the hydrocarbon products of the stoichiometric reaction of CH_3I and $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ are very similar to that of the products in the catalytic conversion of methanol over $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ supported on active carbon, indicating that the mechanism of the propagation of the carbon-carbon chain is the same in the two systems.

The results clearly shows that methyl carbenium ions play an essential role in the formation of carbon-carbon bonds. It is worthy of note that hydrocarbon formation is fast in the $\text{CH}_3\text{I}-\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ system even at 423 K. At the same temperature, methanol gives methoxyl group over ZSM-5 and yields dimethyl ether, but not

Table 1 Reaction Products of Reaction of CH_3I and $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$

Temperature/K	423		573		573 **
Reaction time/min	15	30	5	40	
$\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ used/mmol(A)		0.28		0.28	
CH_3I consumed/mmol(B)	0.95	1.04	0.80	1.22	
B/A	3.4	3.7	2.9	4.4	
Carbon atoms in hydrocarbons/mmol(C)	0.83	0.75	0.82	0.81	
C/A	3.0	2.7	2.9	2.9	
Distribution of Hydrocarbons *					
CH_4	0	0.2	6.3	5.9	6.8
C_2H_4	0.1	0	10.5	7.9	16.6
C_2H_6	—	—	—	—	0.6
C_3H_6	0.3	0.7	21.2	10.8	18.7
C_3H_8	0	0	8.4	28.3	5.6
C_4H_8	11.9	17.3	21.2	15.9	33.9
C_4H_{10}	33.7	34.1	12.5	17.8	
C_5	23.2	23.0	13.5	10.0	10.6
C_6	8.2	9.9	6.3	3.3	
C_7	18.2	13.9	0.1	0.1	7.2
C_8	4.3	0.9	0	—	

* Distributions were calculated on carbon-number basis exclusive of ethane used as an internal standard. Separate experiments revealed that ethane yield was negligible at 423 K and 1.0 % at 573 K.

** Hydrocarbon distribution in methanol conversion over $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ supported on active-carbon under the conditions of W/F = 50 g h mol⁻¹ and methanol pressure of 10 x 1.3 kPa.

hydrocarbons. Difference in the temperature required for C-C bond formation in the two systems indicates that the reactivity of CH_3 moiety depends on the chemical environment, where CH_3 moiety is located. The less reactive CH_3 in methoxyl groups in ZSM-5 need higher temperature to be reactive enough to attack on C-H bonds, in comparison with incipient CH_3^+ from by the stoichiometric reaction.

REFERENCES

- (1) Chang, C. D., and Silvestri, A. J., *J. Catal.*, **47**, 249 (1977)
- (2) Kaeding, W. W., and Butter, S. A., *J. Catal.*, **61**, 155 (1980)
- (3) Kagi, D., *J. Catal.*, **69**, 242 (1981)
- (4) Ono, Y., and Mori, T., *J. Chem. Soc., Faraday Trans. I*, **77**, 2209 (1981)
- (5) Olah, G. A., Klopman, G., and Schlosberg, R. H., *J. Am. Chem. Soc.*, **91**, 3261 (1969)
- (6) Olah, G. A., DeMember, J. R., and Shen, J., *J. Am. Chem. Soc.*, **95**, 4952 (1973)
- (7) van den Berg, J. P., Wolthuizen, J. P., and van Hooff, J. H. C., "Proceedings 5th Internat. Conf. on Zeolites, Naples, 1980" (L. V. Ree, Ed.) p.649, Hayden, New York, 1980
- (8) Zatorski, W., and Kryzanowski, S., *Acta Phys. Chem.*, **24**, 347 (1978)
- (9) Chen, N. Y., and Reagan, W. J., *J. Catal.*, **59**, 123 (1979)
- (10) Ono, Y., Imai, E., and Mori, T., *Z. Phys. Chem., N.F.*, **115**, 99 (1979)
- (11) Anderson, J. R., Mole, T., and Christov, V., *J. Catal.*, **61**, 477 (1980)
- (12) Baba, T., Sakai, J., and Ono, Y., *Bull. Chem. Soc. Jpn.*, **55**, 2657 (1982)